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INDUSTRIAL WASTE SURVEY REPORT, APRIL 28 TO MAY 5, 1953

Environmental Health Center
Cincinnati, Ohio

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INDUSTRIAL WASTE SURVEY REPORT

Archer-Daniels-Midland Company
Chemical Products Division
Wyandotte, Michigan

April 28 to May 5, 1953

U. S. DEPARTMENT OF
HEALTH, EDUCATION, AND WELFARE
Public Health Service
Environmental Health Center
Cincinnati, Ohio

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I. GENERAL INFORMATION

1. Organization of Survey

This survey was a cooperative study conducted by the Chemical Products Division of Archer-Daniels-Midland Company, Wyandotte, Michigan, the Michigan Water Resources Commission, and the Environmental Health Center of the Public Health Service.

Analytical determinations were performed by Public Health Service Chemists in a mobile laboratory located on the grounds of the Wayne County Sewage Treatment Plant at Wyandotte.

Personnel of the Chemical Products Division of Archer-Daniels-Midland Company aided the field survey staff in becoming familiar with liquid waste sources, supplied pertinent data, and furnished materials and labor for hydraulic works.

2. Dates of Survey

April 28 to May 5, 1953.

3. Purpose of Survey

This survey was conducted to determine the characteristics of the process wastes and the residual pollution load discharged from the plant to the Detroit River and to study the efficiency of the large trap handling the bulk of the plant's water-carried wastes. This project was a part of the continuing study of boundary waters pollution being conducted for the International Joint Commission.

4. Personnel Participating

Chemical Products Division of Archer-Daniels-Midland Company

C. Grasiani, Plant Manager
D. Rice, Plant Engineer
C. Luke, Assistant to Plant Engineer

Public Health Service

D. M. Taylor, Public Health Engineer
S. Soneda, Assistant Sanitary Engineer
C. Shadix, Chemist
S. Pinkoski, Chemist
C. Hirth, Chemist
P. Jones, Engineering Aide
M. D. Currey, Laboratory Assistant

5. Location of Plant

This plant of the Chemical Products Division, Archer-Daniels-Midland Co. is located at 4655 Biddle St., Wyandotte, Michigan, on the west bank of the Trenton Channel of the Detroit River.

6. Raw Materials

The principal raw materials are crude vegetable and marine oils. The average weekly consumption of raw materials was about one million pounds.

7. Production

The plant produces hydrogenated glycerides and fatty acids, free fatty acids, and glycerine. Production was approximately one million pounds per week.

8. Operations

The plant operates 24 hours per day, 5 days per week. Packaging is done on Saturdays (6th day).

9. Employees

The number of employees is about 150.

10. Water Supply

Wyandotte city water is used for sanitary purposes, processing, and indirect cooling. Usage for the week beginning April 20, 1953, was 637,000 gallons, and 575,000 gallons for the week of April 27, 1953.

Detroit River water is used for cooling. Approximately 25 per cent of it is used for cooling packaging equipment and is discharged directly to the sewers. Most of the remainder is used in barometric condensers. River water usage for the week beginning April 20, 1953, was 6,413,000 gallons, and 7,637,800 gallons for the week of April 27, 1953.

11. Sewers

Industrial liquid wastes are discharged through the Pennsylvania Salt Manufacturing Company sewers into the Detroit River. Cooling water flows directly to the outfall sewers, but process wastes, including barometric condenser water, pass through separators before entering the sewers.

12. Sanitary Wastes

Sanitary wastes are discharged to the Pennsylvania Salt Manufacturing Co. sewers and thence to the Wyandotte municipal sewer system.

II. MANUFACTURING PROCESS

The manufacturing process has been fully described in a report of a survey conducted by the Michigan Stream Control Commission in February, 1947. It has also been discussed in a Public Health Service memorandum, dated September 15, 1947. There have been only a few minor changes since those dates. Operations consist essentially of processing vegetable and marine oils to produce hydrogenated glycerides and fatty acids, free fatty acids, and glycerine. Figure 1 is a process flow diagram. The processes are briefly described in the following paragraphs.

13. Saponification

The crude oils are first treated with sodium hydroxide to saponify free fatty acids and separate them from the oils.

14. Oil Refining

The alkalized oils are washed with water several times to remove soaps, these water washings being discharged directly into an oil trap (#2). The crude oils are then dewatered in a vacuum evaporator, with vacuum being maintained by a barometric condenser. This condenser discharges into an oil trap (#2). The dewatered oils are then bleached with such materials as carbon black, Fuller's earth, and bentonite.

15. Catalytic Hydrogenation (hardening)

The refined oils are next hydrogenated at high temperature (400°C) and pressure, in the presence of finely divided nickel (catalyst). Some of the hardened oils are cooled, packaged (as solids), and sold.

16. Hydrolysis (splitting)

The major portion of the hydrogenated oils is hydrolyzed in an autoclave with high-pressure steam, forming free fatty acids and glycerine (a 10 to 12% glycerine water known as "sweet water"). Any oils lost through safety valves are discharged to a trap (#3). Condensed vapors from pressure equalizer tanks (located between autoclaves and separation tanks) are discharged to a trap (#4). The fatty acids are separated by gravity from the glycerine water in tanks.

17. Glycerine Recovery

Glycerine water from the bottom of the separators is pumped through deionizers to remove contaminants and then concentrated in a vacuum evaporator. Barometric condenser water from the vacuum evaporator flows to the main trap. The dewatered glycerine is decolorized and shipped.

18. Fatty Acid Purification

The crude fatty acids are vacuum distilled to form pure acids and pitch, which are sold. Barometric condenser water, carrying considerable entrained matter, is discharged to traps (#3 and #4). The distilled fatty acids are sprayed into cooling towers to form solid granular products, which are marketed. The free acids may be hydrogenated before cooling and packaging.

19. Soapstock Splitting

The soaps washed out of the crude oil in the early operations of oil purification along with soap liquors from soap manufacturers, are treated with sulfuric acid to form free fatty acids. The poor quality acidified soaps may be hydrolyzed by the Twitchell process to increase fatty acid formation. These acids are then vacuum distilled, cooled, and packaged. Hydrogenation is optional.

The better quality, more pure, and more highly saturated, acidified soapstocks, are dewatered, bleached, hydrogenated, autoclaved, and distilled, as described for crude oil processing.

III. WASTE SOURCES

Sanitary wastes are discharged directly to Pennsylvania Salt Manufacturing Company sanitary sewers. Indirect cooling water is discharged directly to outfall sewers without treatment. Barometric condenser water and process water are discharged to small traps whose effluents flow through a large separator before entering the sewers of the Pennsylvania Salt Manufacturing Co. The effluent from one small trap and overflow from another discharge directly to the sewers without passing through the main separator.

The main sources of liquid wastes are shown in Figure 1. They are as follows:

(1) Process Wastes to Trap 1

A. Acid waste from acid splitting.

B. Acid and glycerine waste from Twitchellizing (hydrolysis) process.

(2) Process Wastes to Trap 2

A. Soap washings from saponification (sodium hydroxide treating) of oils.

B. Barometric condenser water from vacuum evaporator, dewatering crude oils.

(3) Process Wastes to Trap 3

A. Oil lost through pop-off valve on autoclave.

(4) Process Wastes to Trap 4

A. Blow-off from equalizing tank.

(5) Process Wastes to Traps 1 or 4

A. Barometric condenser water from fatty acid vacuum stills.

(6) Process Wastes Not Flowing Through Traps Before Entering Main Separator

A. Barometric condenser water from glycerine vacuum evaporator.

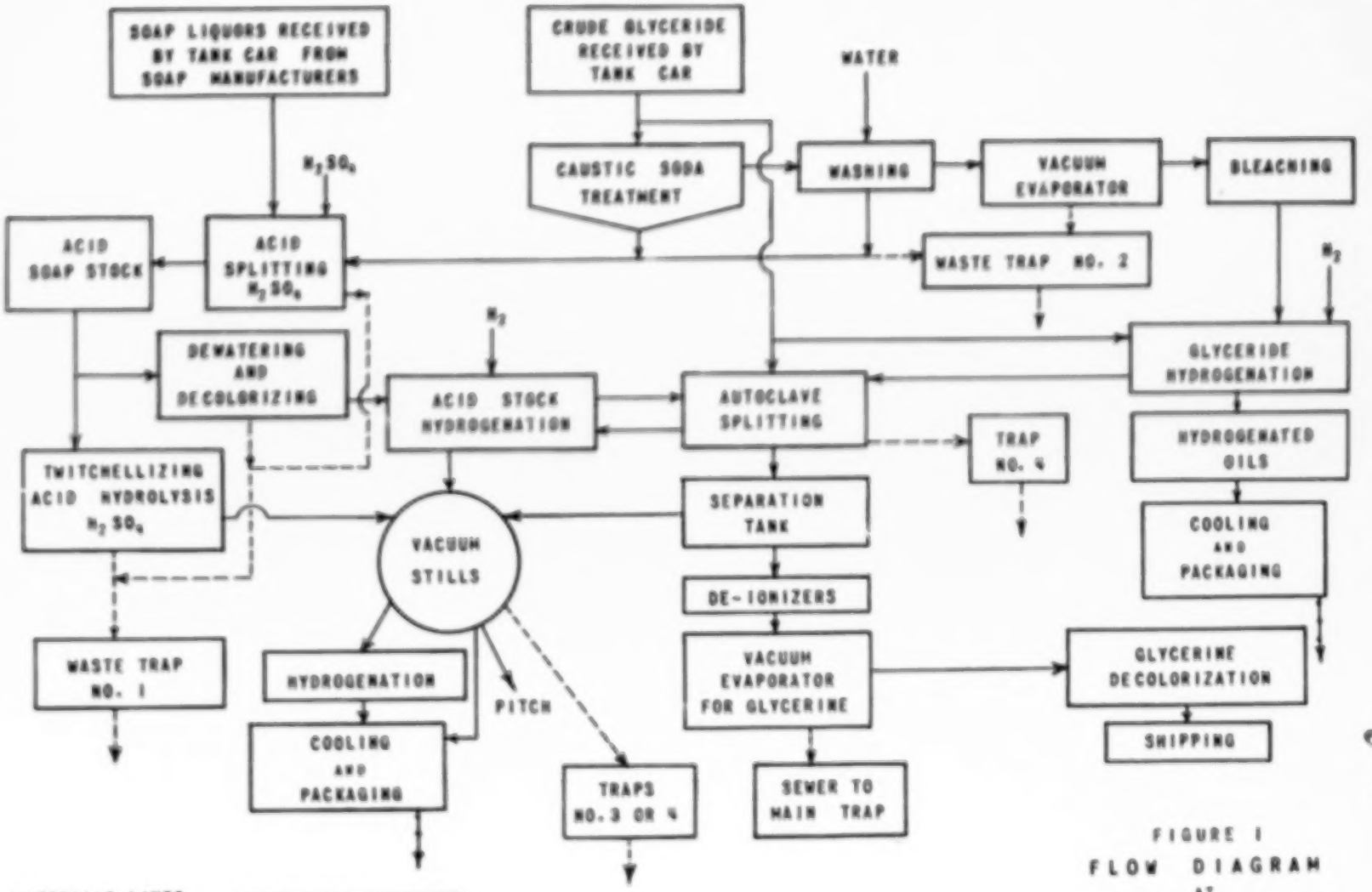

FIGURE I

FLOW DIAGRAM

AT

CHEMICAL PRODUCTS DIVISION

ARCHER -DANIELS- MIDLAND

WYANDOTTE, MICHIGAN

ENVIRONMENTAL HEALTH CENTER

6-a

IV. REMEDIAL MEASURES FOR WASTES

The original small traps have been supplemented with a relatively large separator (See Figure 2). Floating materials, which are mostly organic products, are periodically skimmed off and recovered. Settleable solids are removed, about once a year, from the bottom.

Flow-through tests were made on the two sections of the main trap, using Congo red dye. Based on the tank dimensions (10' -8" x 23' x 6' deep) and the measured flows (0.6 MGD for east side and 0.43 MGD for west side), the theoretical detention time in the two sections of the main trap would be 26-27 minutes in the east side and 37-38 minutes in the west side. Concentrated dye solution was dumped into the inlet stream and the time recorded for its appearance at the outlet end. It took two minutes for the dye to flow through both sections. The maximum intensity of dye color appeared at the outlet end of the east section in 4-5 minutes, while the time for the west section was 5-6 minutes. All of the dye color disappeared from the east section in about 30 minutes, while it took 60 minutes for it to disappear from the west section outlet. The whole surface of the east section was colored red at one time, but only the inlet and outlet surfaces of the west section were ever colored by the dye.

The engineering department stated that the bottom baffles had not been operating satisfactorily and they had been removed. The top baffle at the inlet end of the west section had also been removed.

A rotameter has been installed on the acid feed line to the soap stock splitter and hydrolyzer to avoid excessive use of sulfuric acid. This device should prevent low pH's in the plant effluent.

V. PRODUCTION

The material through-puts in the units in the various departments for the week of April 27, 1953, were as follows:

Refining operation	773,000 lb oil
Old plant hydrogenation	898,000 " "
New plant hydrogenation	300,000 " "
Splitting operation	1,014,000 " "
Distilling operation	860,000 " "

For comparison, the monthly through-puts in these departments for the month of February, 1953, were as follows:

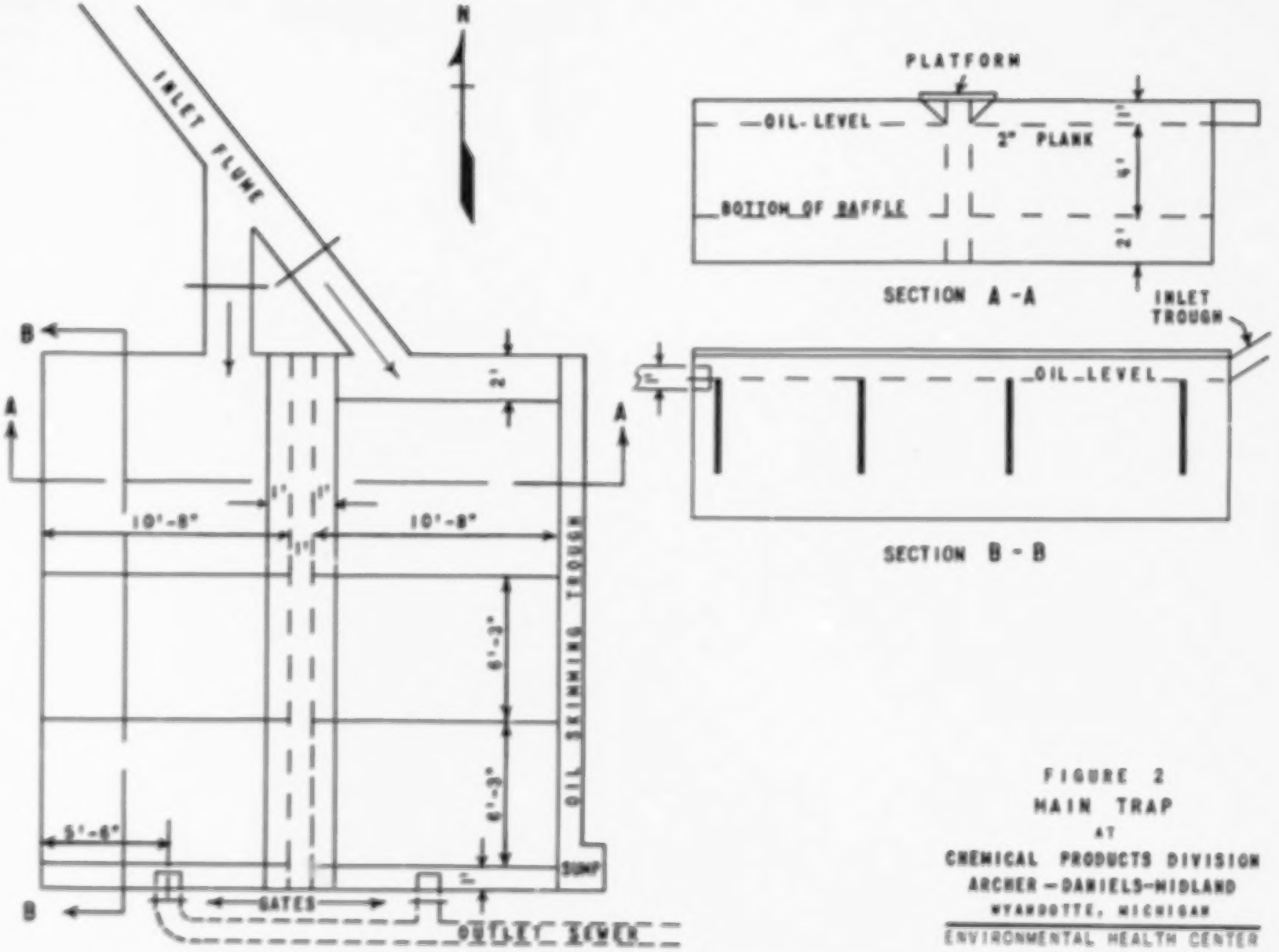

FIGURE 2
MAIN TRAP
AT
CHEMICAL PRODUCTS DIVISION
ARCHER-DANIELS-MIDLAND
WYANDOTTE, MICHIGAN

ENVIRONMENTAL HEALTH CENTER

Refining operation	2,480,000	lb oil
Old plant hydrogenation	3,050,000	" "
New plant hydrogenation	1,045,000	" "
Splitting operation	3,060,000	" "
Distilling operation	2,780,000	" "

The pounds of oil processed in the splitting operation indicate approximately the production rate.

VI. SURVEY PROCEDURE

20. Sample Collection

Plant operations were more or less continuous. Automatic level recorder records indicated fairly constant waste flows and equal portions of samples were taken for compositing. Separate samples were composited in one-liter glass-stoppered bottles for the oil determination. Samples were collected at 30-minute intervals over 8-hour periods from 8:00 A.M. to 4:00 P.M. They were collected from the following points at the time of the survey:

(1) Raw Water - for purpose of obtaining net quantities of waste constituents.

(2) Influent line to main separator.

(3) Effluent line from east section of main separator.

(4) Effluent line from west side of main separator.

(5) Effluent line from small trap on waste line from specialty still - discharging directly to outfall sewer without passing through main separator.

(6) Overflow from trap, on east side of new building, discharging directly to outfall sewer.

21. Flow Data

(1) Water consumption by the plant was metered.

(2) The baffles in front of the outlet pipes of the two sections of the main trap were only a few inches in front of the pipes. It was necessary to install weir boxes around the outlet pipes with two 9-inch partially contracted rectangular weirs for each section. Flows were estimated with automatic level recorders.

(3) A 2-ft contracted rectangular weir was installed in the pilot still effluent trap. Flows were estimated from automatic level recorder charts.

22. Laboratory Analyses

The following laboratory determinations were made on the samples:

(1) Total solids.

(2) Total volatile matter.

(3) Total suspended solids.

(4) Total suspended volatile matter.

(5) B.O.D. - 5-day at 20°C.

(6) Oils.

(7) pH.

(8) Acidity

The procedures followed in making the determinations, with the exception of oils, were those given in "Standard Methods for the Examination of Water and Sewage," 9th Edition. The procedure for oils is given in "Analytical Methods for Boundary Waters Quality Control" by the Board of Technical Advisers to the International Joint Commission.

VII. EXPLANATION OF ANALYSES

A brief explanation of the various laboratory determinations is given to serve as an aid in the interpretation of the analytical results reported.

23. Solids

Suspended solids are insoluble solids which float on the surface of the liquid, remain in suspension, or settle out on standing. They are determined by filtering samples through asbestos mats in Gooch crucibles. Total solids consist of all the solids in a sample which do not volatilize at 103° C or less. They include both suspended

and dissolved solids. Volatile solids, or volatile matter, are those solids in the sample which are lost on ignition at a temperature of 600°C for 15 minutes.

Suspended solids cause water to appear turbid and unsightly. Settleable suspended solids are objectionable because they cause silting and sludge banks. Suspended solids are particularly objectionable in water supplies used for domestic and industrial purposes. Relatively large amounts of dissolved solids may be objectionable in domestic water supplies for physiological reasons, and in industrial water supplies for process reasons. The volatile solids (matter) results are obtained by an empirical method but they are intended to indicate the organic material content of the solids.

24. B.O.D.

The biochemical oxygen demand of sewage, polluted waters, or industrial wastes, is the oxygen (in ppm) required during stabilization of the decomposable organic matter by aerobic bacterial action. The rate of oxygen demand is dependent on both time and temperature and consequently the standard conditions of 5 days' incubation at 20°C are usually used for the test. Approximately 68 per cent of the oxygen demand of the carbonaceous material present in normal domestic sewage is satisfied under the conditions of 5 days' incubation at 20°C. The oxygen demand rates of industrial wastes, however, may or may not follow the typical oxidation curve for domestic sewage. It would be necessary to incubate a particular sample of waste for such a period of time that no more oxygen demand was exerted, in order to determine the total B.O.D.

High B.O.D. values are objectionable from a stream pollution standpoint because they reduce the oxygen resources of the streams, adversely affecting the aquatic life. If the oxygen content is depleted, anaerobic conditions develop and the water is rendered undesirable for supply and recreational purposes.

25. Oils

The oil results were obtained by extracting the samples with a 1:1 mixture (by volume) of diethyl ether and carbon tetrachloride. These results represent all of the materials which are soluble in these organic solvents, and not just the true oils as such.

Oily materials are objectionable from the standpoint of stream pollution because they are unsightly, damaging to wildlife and

aquatic life, detrimental to recreational facilities, and interfere with treatment processes for public and industrial water supplies. Oily films on the surfaces of lakes and streams interfere with the normal reaeration of the water and may be difficult to remove. Certain sludges may contain oily materials which may be toxic to bottom fauna and flora.

26. pH

The symbol "pH" denotes the negative logarithm of the hydrogen-ion normality. The pH value indicates the relative acidity or alkalinity of a solution, being lower with higher degrees of acidity.

pH data are helpful in measuring the effects of acid and alkaline wastes on natural surface waters. Acids causing pH values below 4.0 and alkalies causing pH values above 10.0 are undesirable and hazardous for fish life in waters which are not naturally so acid or alkaline. pH is also an important factor when considering treatment for domestic and industrial water supplies.

27. Acidity

The acidity of a water is usually caused by the presence of uncombined carbon dioxide, mineral acids, and salts of strong acids and weak bases. Industrial wastes may contain acid materials capable of producing hydrogen ions in solution. The amount of acidity is determined by titration with a standard solution of a strong base to a definite equivalence point as given by indicator solutions. Methyl orange indicator (pH approximately 4.0), or its equivalent, is used to obtain this equivalence point for the "mineral acid acidity." Phenolphthalein or its equivalent (pH 8.1 -8.2) is used to obtain the equivalence point for total acidity. Total acidity includes mineral acid acidity. Acidity results are expressed as ppm calcium carbonate.

The common strong mineral acids (H_2SO_4, H_2SO_3, HCl, and HNO_3) can be directly lethal to fish in most natural waters when the pH is 5.0 or lower. A number of weak inorganic and organic acids can impart to some waters pronounced toxicity for fresh-water fish without lowering the pH to a value as low as 5.0. The toxicity under these conditions is attributable chiefly to the undissociated acid or acid gas in solution, or to the anions or salts of the acid involved. Sulfurous acid is included in this last group. The pH value alone may not be regarded as a reliable index of dangerous pollution of water with one of the acids of this group. Both the concentration and the pH of the solution usually must be considered.

VIII. DISCUSSION OF RESULTS

28. Characteristics of Wastes

Daily analytical results, showing gross and net concentrations of waste constituents, are given in Table 1. The raw river water to the plant was analyzed for the purpose of obtaining net values. The B.O.D. values for the raw water were unusually low and may have been due to some toxic effect.

Average, daily, gross and net quantities of waste constituents, discharged from the traps to the sewers, are shown in Table 2. There was a very small flow in the overflow line from the new building. Qualitative results were obtained for this line but flow measurements were not made. For all practical purposes, however, the total quantities of wastes shown in Table 2 represent the quantities of significant waste constituents discharged from the plant.

Suspended volatile matter constitutes most of the volatile matter in the wastes, indicating most of the organic materials are in the suspended solids.

29. Main Trap

The influent to the main trap is not equally divided between the two sections, which operate in parallel. The waste removal efficiencies, for the period of the survey, are as follows:

Waste Removal Efficiencies of Two Sections of Main Trap - Per Cent

Waste Constituent		East Section	West Section	Average Total
Flow - MGD		0.60	0.43	1.03
B.O.D.	April 28	27	61	
	29	18	58	
	30	0.9	66	
	May 4	-10*	56	
	Average	9	60	30
Susp. Solids	April 28	5.4	58	
	29	49	75	
	30	12	67	
	May 4	- 8.2*	58	
	Average	15	65	36
Oils	April 28	29	68	
	29	41	67	
	30	9.9	79	
	May 4	4.3	65	
Average		21	70	41

* Negative values indicate increases rather than decreases. It is not reasonable to expect negative results, but the river level was up on May 4, causing a backing-up in the sewers which may have influenced the sampling point.

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Cinti., Ohio

Table 1 - Daily, Gross and Net Concentrations of Waste Constituents, - p.p.m.

Archer-Daniels-Midland, Wyandotte, Michigan

Date 1953	B.O.D. 5-day		Total Solids		Total Vol. Matter		Suspended Solids		Susp. Vol. Matter		Oils		pH	Acidity Mineral		Acidity Total	
	Gross	Net	Gross	Net	Gross	Net	Gross	Net	Gross	Net	Gross	Net		Gross	Net	Gross	Net
Influent to Main Traps																	
April 28	321	321	814	282	297	221	241	217	208	204	213	208	6.9				
29	268	268	874	459	349	277	512	459	349	277	273	269	6.0				
30	335	335	2080	1670	549	470	328	310	328	310	233	232	2.5	370	370	530	530
May 4	271	271	620	127	278	127	183	127	158	127	186	183	7.2				
Average	300	300	1100	630	370	270	320	280	260	230	230	220					
Effluent from West Trap																	
April 28	125	125	611	79	157	79	100	76	81	76	69	64	7.6				
29	113	113	532	117	180	108	126	107	114	105	89	85	7.1				
30	115	115	534	124	137	58	109	91	100	58	50	49	6.9				
May 4	118	118	491	64	165	64	77	23	67	23	66	63	7.3				
Average	120	120	540	96	160	78	100	74	91	66	69	65					
Effluent from East Trap																	
April 28	234	234	747	215	276	200	228	204	186	182	152	147	7.1				
29	220	220	632	217	260	188	259	217	232	188	162	158	6.8				
30	332	332	2060	1650	580	501	289	271	289	271	210	209	2.5	397	397	561	561
May 4	300	300	676	183	255	153	198	144	172	144	178	175	6.9				
Average	270	270	1030	570	340	260	240	210	220	200	180	170					
Pilot Still Effluent																	
May 4	486	486	684	191	240	138	336	191	240	138	332	329	8.0				
5	178	178	523	63	214	63	138	63	136	63	110	107	7.3				
Average	330	330	600	130	230	100	240	130	190	100	220	220					
Overflow from Traps at New Building, Flowing Directly to Sewers																	
May 4	61	61	483	75	177	75	41	0	28	0	24	21	8.0				
5	27	27	466	25	107	25	35	6	28	6	13	10	7.9				
Average	44	44	470	50	140	50	38	3	28	3	19	16					
Raw Water to Plant																	
April 28	0.08		532		76		24		4		4.6		8.4				
29	.02		415		72		19		9		3.8		8.4				
30	.02		410		79		18		9		1.2		8.4				
May 4	.12		493		102		54		21		2.9		8.5				
Average	0.06		460		82		29		11		3.1						

Table 2 - Average, Gross and Net Quantities of Waste Constituents - Pounds per Day

	Influent to Main Trap	East Section Effluent	West Section Effluent	Total from Main Trap	Pilot Still Effluent	Total from Plant
	Pounds per Day					
Flow - MGD	1.03	0.60	0.43	1.03	0.096	1.126+ *
B.O.D., 5-day						
Gross	2580	1350	430	1780	240	2020
Net	2580	1350	430	1780	240	2020
Total Solids						
Gross	9450	5150	1940	7090	430	7520
Net	5420	2850	340	3190	100	3290
Total Volatile Matter						
Gross	3180	1700	580	2280	170	2450
Net	2320	1300	280	1580	80	1660
Suspended Solids						
Gross	2750	1200	360	1560	170	1730
Net	2400	1050	270	1320	100	1420
Suspended Volatile Matter						
Gross	2230	1100	330	1430	160	1590
Net	1970	1000	240	1240	80	1320
Oils						
Gross	1980	900	250	1150	160	1310
Net	1890	850	230	1080	160	1240

* The volume of flow from the traps at the new building, directly to the sewers, was not known. The given values should be increased slightly to account for the wastes from this source.

Not only were the waste constituent removal efficiencies greater for the west section than for the east section, but they were more uniform.

30. Specialty Still Effluent Trap

It was stated by management that this still only operated about three months out of the year. Ignoring the wastes from the overflow line at the new building, wastes from the trap handling the specialty still effluent constitute the following percentages of the net, total plant wastes: 5-day B.O.D. 12%, total solids 3%, total volatile matter 5%, suspended solids 7%, suspended volatile matter 6%, and oils 3%.

IX. SUMMARY

(1) This plant processes crude vegetable and marine oils to produce hydrogenated glycerides and fatty acids, free fatty acids, and glycerine. Production for the period of the survey was approximately one million pounds per five-day week.

(2) Sanitary wastes are discharged to the Wyandotte municipal sewers.

(3) Uncontaminated cooling water is discharged directly through outfall sewers to the Detroit River.

(4) Process and barometric condenser water wastes are passed through traps before discharge to the Detroit River. About 92 percent of the waste flow finally passes through a large separator before discharge to the river. The remainder is discharged from two small sewers directly to outfall sewers.

(5) The main separator has two sections (each 10'-8" x 23' x 7' deep). These sections operate in parallel but inlet design is such that normal flows through them are not equal. Average significant waste constituent removals in the two sections are as follows:

Waste Constituent	East Section	West Section	Weighted Average Total
	Per	Cent	
B.O.D. - 5-day	9	60	30
Suspended solids	15	65	36
Oils	21	70	41
Flow - MGD	0.60	0.43	1.03

Total waste removal efficiency of the main separator should be increased by equalizing the flows to the two sections and properly adjusting the baffles.

(6) The total net quantities and unit net quantities of waste constituents discharged daily from the plant are as follows:

Waste Constituent	Total Net Quantities lb/day*	Unit Net Quantities lb/ton product**
B.O.D. - 5 day	2020	20.2
Total solids	3290	32.9
Total volatile matter	1660	16.6
Suspended solids	1420	14.2
Suspended volatile matter	1320	13.2
Oils	1240	12.4
Flow - Gallons	1,126,000	11,260

* Not including small amount of wastes in overflow line from new building.

** Eighty-eight per cent of the net total B.O.D., 93 per cent of the net total suspended solids, and 87 per cent of the net total oils, are discharged from the main separator.